A High Resolution Study of Low Lying Correlation Satellites in Xenon

R.C. Shiell[1], M. Evans[2], S. Stimson[2], C-W. Hsu[3], C.Y. Ng[2] and J.W. Hepburn[1]

[1]Chemistry Department, University of Waterloo, Waterloo, Ontario N2L 3G1 Canada
[2]Ames Laboratory, USDOE and Department of Chemistry,
Iowa State University, Ames, IA 50011, USA
[3]Chemical Science Division, Ernest Orlando Lawrence Berkeley National Laboratory,
University of California, Berkeley, CA 94720, USA

ABSTRACT

The technique of pulsed field ionization - zero kinetic energy photoelectron spectroscopy, typically applied to the investigation of ionic states in atoms and molecules resulting from single electron excitation, has been used to probe the correlation satellite states of xenon between 23.6-24.7 eV. The resulting spectra show the formation of clearly resolved satellite states with intensities of similar magnitude to that of the $5s5p^6$ $^2S_{1/2}$ ionic state. This technique can be extended to other atomic and molecular species to obtain the positions and cross-sections for formation of such states.

INTRODUCTION

As the energy of light incident upon an atom or molecule is increased above that of the lowest ionization energy a variety of neutral and ionic electronic states can be formed. The former include singly excited states converging onto an ion state with one hole in an inner orbital and doubly excited states converging onto an ionic (satellite) state with two electrons excited from the neutral configuration. These neutral resonances may decay to lower lying ionic states through the process of autoionization. The ionic states include single hole and satellite ionic states formed directly in conjunction with a free electron. Probing the formation and characteristics of these ionic states is a primary aim of photoelectron spectroscopy. In traditional photoelectron spectroscopy the photon energy is scanned and all electrons formed with a specific kinetic energy and angular distribution are detected. Threshold photoelectron spectroscopy uses static electric fields to allow the selective detection of electrons with near-zero kinetic energy formed in conjunction with a cationic state. Satellite states can be difficult to probe using this technique; in general such states are formed at high photon energies, they produce low signal intensities, and they contribute to a highly congested spectrum. The introduction of pulsed-field ionization zero kinetic energy (PFI-ZEKE) photoelectron spectroscopy in recent years[1] has largely overcome this problem and enabled a high-resolution spectroscopic probe of ionic states formed by excitation and subsequent field ionization.

The formation of singly-excited neutral or ionic states may be understood by invoking the single particle model whilst formation of neutral doubly excited or satellite states is forbidden within this approximation and is solely the result of the correlated motions of electrons within the species. It has been useful in the past to separate the correlation effects that result in the formation of satellite states into 'intrinsic' and 'dynamic' in regard to their threshold behavior[2] and deducing from this behavior the dominant correlations contributing to the intensity of a given satellite.

Calculations beyond the single-particle approximation in xenon that predict satellite positions and intensities are particularly challenging due to large relativistic effects and strong mixing between configurations. The Xe satellite spectrum has previously been measured over a wide incident photon energy range from the near-threshold[3] to the x-ray[4] regions using traditional photoelectron spectroscopy and the partial strengths of various ionic states have been obtained. Formation of an

ionic state with one hole in its core results in a 'main line' peak at specific energy in the photoelectron spectrum, whilst formation of a satellite state results in a peak on the low kinetic energy side of a main line peak. The resolution with which low lying satellite states have been observed is typically 50 meV at photon energies of 40.8 eV,[5] 130 meV at energies less than 100 eV,[6] and 300 meV at 1.487 keV.[4] In the region containing the lowest-lying satellite states of xenon 8 ionic states are known to exist from 23.6-24.7 eV, with some separated by an energy as small as 5 meV.[7] Obtaining the partial strengths of each ionic state at any photon energy is therefore often complicated by the fact that there are many unresolved satellite states belonging to different symmetry manifolds within the spectra. A high resolution light source and detection technique is required to unambiguously determine partial strengths for each ionic state formation at a particular photon energy. We report the use of a high resolution spectrometer at the Chemical Dynamics Beamline[8] at the Advanced Light Source (ALS) to detect and obtain the relative intensities of formation of the 5s main line peak and 7 satellite states of xenon.

EXPERIMENTAL

The spectrometer has been discussed in detail elsewhere[8] and so only an outline will be given here. The atomic beam was formed by a supersonic expansion of 99.999 % (research grade) xenon at a stagnation pressure of 500 Torr through a metal nozzle of 0.127 mm diameter at 298 K. The ALS was operated in multi-bunch mode, with 304 light bunches within 608 ns followed by a dark gap of 48 ns, forming one ring period. As the photon energy was scanned across high-lying states that converge to an ionic state, Rydberg states of xenon containing one highly-excited electron were formed. Below the threshold for the $5s^{-1}$ state at 23.397 eV these Rydberg states were singly excited and below each threshold for satellite formation (e.g. the $5s^2 5p^4(^3P)6s\ ^4P_{5/2}$ ion state at 23.669 eV) they were doubly-excited states containing one high-lying electron. During every alternate dark gap a 40 ns pulsed electric field of 0.67 V/cm was applied to the interaction region, field ionizing those states formed within 4 cm^{-1} of an ionic limit[9], and accelerating the resulting near-threshold electrons towards a tandem steradiancy-hemispherical analyzer for selective detection. By calibrating the photon energy scale using the ionization onsets of neon and helium, the positions of the lines were found to be at their expected positions within experimental uncertainty (0.5 meV) and more exact energy calibration was done by comparison with the known optical data[7].

RESULTS

Figure 1 shows a split energy scale spectrum of the observed ionic states formed due to PFI in xenon. Within the energy range sampled the 5s main line peak (the $5s5p^6\ ^2S_{1/2}$ state) and seven of the eight known satellite peaks were observed. We did not observe the $5s^2 5p^4 5d\ ^4F_{9/2}$ state and conclude its intensity is less than that of the observed $5s^2 5p^4 5d\ ^4D_J$ states.

An expanded view of the observed $5s^2 5p^4 5d\ ^4D_J$ states is given in Figure 2, which show a full width at half maximum (FWHM) of 0.9 meV. The intensities of all peaks have been calculated by computing the areas under the peaks after correcting for the background and are displayed (relative to the $5s5p^6\ ^2S$ main line peak with magnitude 100) in Table 1. The experimental error in each satellite intensity, due to variations in conditions and statistical fluctuations, is estimated to be from 20% to 30%, with the higher values for the less intense peaks. For comparison the reported relative peak heights of these satellite states formed from unpolarized He II light at 40.8 eV [5] and polarized synchrotron light at 63.5 eV [10] are shown in Table 1. It should be noted that the former is not taken at the magic angle with respect to the beam (see ref. 6 for details) and thus could show a maximum difference by a factor of four from the true relative cross-sections of some states. Also
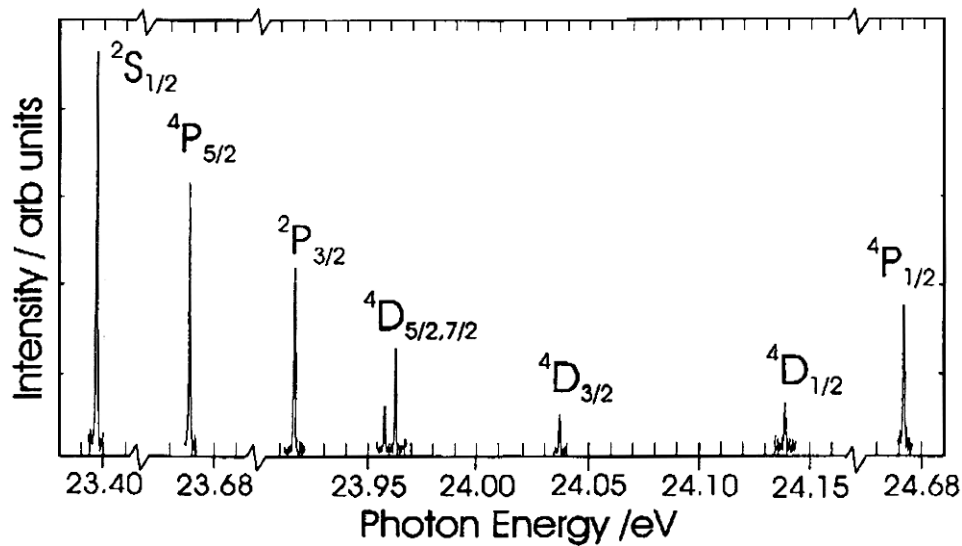
Figure 1. A split-energy spectrum with consistent energy scale, normalised by photon flux, of the ionic states in xenon observed through PFI-ZEKE photoelectron spectroscopy. The main line state at 23.397 eV is shown and seven correlation satellites. The position of each peak is calibrated from the analysis by Hansen and Persson [7] and labeled with LS notation, see text.
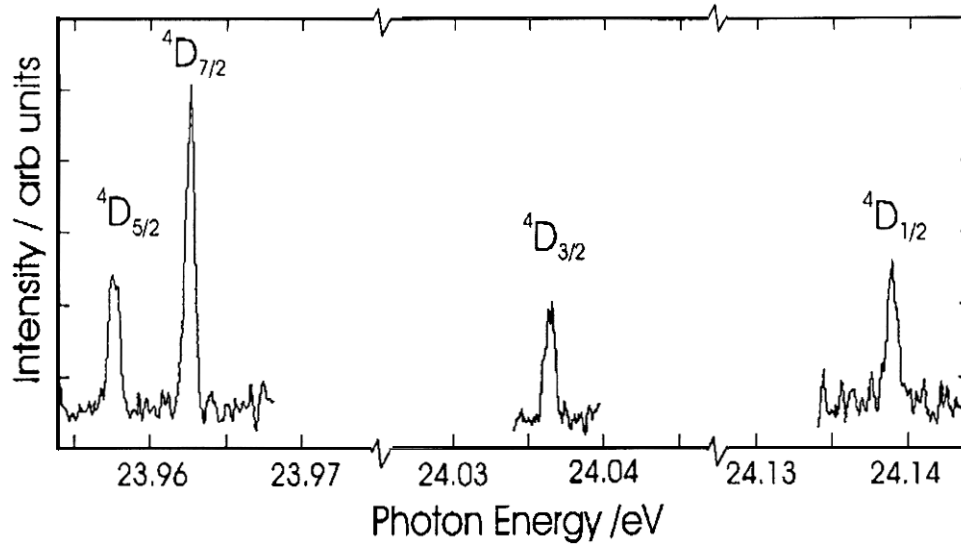

Figure 2. A split-energy spectrum with consistent energy scale, normalised by photon flux, of the four satellite states belonging to the $5s^25p^45d$ ^4D_J manifold, showing the width of each peak to be 0.9 meV.

shown are the absolute partial ionization cross-sections of the satellites, calculated from our intensity data. These were obtained by scaling the 5s photoionization cross-section data of Samson and Gardner[11], which was recorded at photon energies down to 23.6 eV and shows a leveling off towards threshold.

The process which has been observed is one of single or double excitation to a Rydberg state and subsequent removal of the Rydberg electron by the pulsed electric field. At threshold it is apparent that satellite states with high and low J values are formed with equal preference. All such states have intensities not dissimilar to that of the main line peak with those containing the same ionic core having similar intensities. The first two characteristics are noticeable in the lower resolution threshold spectrum of Hall et al.[3], but more detailed comparisons with their work are complicated

TABLE 1. Intensities and cross-sections of nine of the ionic states of xenon with binding energies in the range of 23.3-24.7 eV observed at the thresholds, at 40.8 eV and 63.5 eV.

Ion state[a]	Energy[b] / eV	Relative Intensities[c]			Cross-section at threshold[e] / Mb
		at threshold (this work)	at 40.8 eV[d] (ref 5)	at 63.5 eV (ref 10)	
$5s5p^6(^2S_{1/2})$	23.3967	100	100	100	0.50
$(^3P)6s(^4P_{5/2})$	23.6689	54	0.21	-	0.27
$(^3P)6s(^2P_{3/2})$	23.9164	55	0.76	0.2	0.28
$(^3P)5d(^4D_{5/2})$	23.9576	15	0.52	-	0.08
$(^3P)5d(^4D_{7/2})$	23.9627	24	0.09	-	0.12
$(^3P)5d(^4D_{3/2})$	24.0366	9.2	0.58	-	0.05
$(^3P)5d(^4D_{1/2})$	24.1388	12	0.23	-	0.06
$(^3P)5d(^4F_{9/2})$	24.4546	-	0.74	0.2	-
$(^3P)6s(^4P_{1/2})$	24.6719	47	2.4	4.8	0.24

a) States given in LS notation. The parental configuration of the satellite states is $5s^25p^4(^3P)$.
b) ref 7.
c) The intensity for the $5s^{-1}$ main line is arbitrarily normalized to 100.
d) Data not taken at the magic angle, see text.
e) Scaled from the data for threshold formation of the $5s^{-1}$ state from Samson and Gardner, ref 11.

by both the number of unresolved states within and possible resonant enhancements contributing to their spectrum.

The trend from low to high photon energies, with the dominant correlations expected to change, can be clearly seen in Table 1. The results at 40.8 eV and 63.5 eV are expected to be intermediate between the two extremes, where most states have not reached their high energy limits and others have already subsided in intensity from their threshold values. Indeed, by 72 eV, data presented by Lagutin et al.[6] show the majority of states observed with binding energy from 23-34 eV correspond to J=1/2 and 2, indicating a strong contribution from the $5s^{-1}$ main line. This becomes more extreme at still higher photon energies, and in the x-ray region states with J=1/2 are exclusively observed[6].

SUMMARY
In summary, we have verified the positions and made the first determination of the relative intensities of the seven observed xenon correlation satellites formed at threshold between 23.6-24.7 eV. The high resolution obtained has allowed determination of the absolute partial cross sections and provides a stringent test for the comparison of theoretical predictions. We expect such studies to be extended to the investigation of a variety of atomic and molecular systems, and to higher-lying satellite states, in the near future.

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Principal investigator: J.W. Hepburn, Chemistry Department, University of Waterloo, Waterloo, Ontario N2L 3G1 Canada. Email: hepburn@uwaterloo.ca. Telephone: (519) 888-4065.